

HYDRAZONE-BASED CHARGE TRANSPORT MATERIALS

5 FIELD OF THE INVENTION

This invention relates to organophotoreceptors suitable for use in electrophotography and, more specifically, to organophotoreceptors having a tetrahydrazone-based charge transport material with two aromatic hydrazone groups, each independently bonded to an arylamine group through a linking group having a
10 hydrazone group.

BACKGROUND OF THE INVENTION

In electrophotography, an organophotoreceptor in the form of a plate, disk, sheet, belt, drum or the like having an electrically insulating photoconductive element on an
15 electrically conductive substrate is imaged by first uniformly electrostatically charging the surface of the photoconductive layer, and then exposing the charged surface to a pattern of light. The light exposure selectively dissipates the charge in the illuminated areas where light strikes the surface, thereby forming a pattern of charged and uncharged areas, referred to as a latent image. A liquid or solid toner is then provided in the vicinity
20 of the latent image, and toner droplets or particles deposit in the vicinity of either the charged or uncharged areas to create a toned image on the surface of the photoconductive layer. The resulting toned image can be transferred to a suitable ultimate or intermediate receiving surface, such as paper, or the photoconductive layer can operate as an ultimate receptor for the image. The imaging process can be repeated many times to complete a
25 single image, for example, by overlaying images of distinct color components or effect shadow images, such as overlaying images of distinct colors to form a full color final image, and/or to reproduce additional images.

Both single layer and multilayer photoconductive elements have been used. In single layer embodiments, a charge transport material and charge generating material are
30 combined with a polymeric binder and then deposited on the electrically conductive substrate. In multilayer embodiments, the charge transport material and charge

generating material are present in the element in separate layers, each of which can optionally be combined with a polymeric binder, deposited on the electrically conductive substrate. Two arrangements are possible for a two-layer photoconductive element. In one two-layer arrangement (the "dual layer" arrangement), the charge-generating layer is deposited on the electrically conductive substrate and the charge transport layer is deposited on top of the charge generating layer. In an alternate two-layer arrangement (the "inverted dual layer" arrangement), the order of the charge transport layer and charge generating layer is reversed.

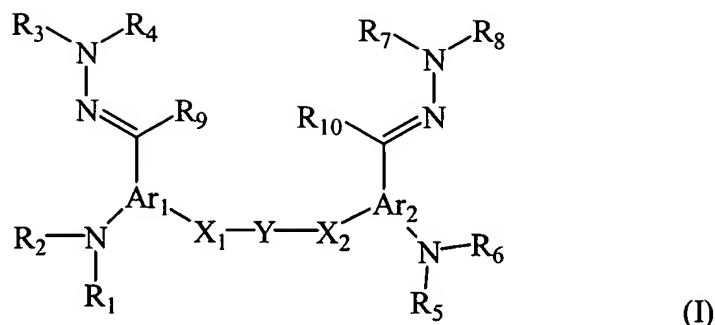
In both the single and multilayer photoconductive elements, the purpose of the charge generating material is to generate charge carriers (i.e., holes and/or electrons) upon exposure to light. The purpose of the charge transport material is to accept at least one type of these charge carriers and transport them through the charge transport layer in order to facilitate discharge of a surface charge on the photoconductive element. The charge transport material can be a charge transport compound, an electron transport compound, or a combination of both. When a charge transport compound is used, the charge transport compound accepts the hole carriers and transports them through the layer with the charge transport compound. When an electron transport compound is used, the electron transport compound accepts the electron carriers and transports them through the layer with the electron transport compound.

SUMMARY OF THE INVENTION

This invention provides organophotoreceptors having good electrostatic properties such as high V_{acc} and low V_{dis} .

In a first aspect, an organophotoreceptor comprises an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(a) a charge transport material having the formula:



where R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 are, each independently, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group;

R_9 and R_{10} are, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group;

Ar_1 and Ar_2 are, each independently, an aromatic group;

Y comprises an arylamine group, such as a carbazole group, a julolidine group, and an (N,N-disubstituted)arylamine group; and

X_1 and X_2 are, each independently, linking groups, such as a $-(CH_2)_m-N(R_{11})-N=C(R_{12})-$ group, where R_{11} and R_{12} are, each independently, hydrogen, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group, m is an integer between 1 and 30, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, or a SiR_eR_f where R_a , R_b , R_c , R_d , R_e , and R_f are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, an alkyl group, an alkoxy group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group; and

(b) a charge generating compound.

The organophotoreceptor may be provided, for example, in the form of a plate, a flexible belt, a flexible disk, a sheet, a rigid drum, or a sheet around a rigid or compliant drum. In one embodiment, the organophotoreceptor includes: (a) a photoconductive element comprising the charge transport material, the charge generating compound, a second charge transport material, and a polymeric binder; and (b) the electrically conductive substrate.

In a second aspect, the invention features an electrophotographic imaging apparatus that comprises (a) a light imaging component; and (b) the above-described

organophotoreceptor oriented to receive light from the light imaging component. The apparatus can further comprise a toner dispenser, such as a liquid toner dispenser. The method of electrophotographic imaging with photoreceptors containing the above noted charge transport materials is also described.

5 In a third aspect, the invention features an electrophotographic imaging process that includes (a) applying an electrical charge to a surface of the above-described organophotoreceptor; (b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of at least relatively charged and uncharged areas on the surface; (c) contacting the surface with a
10 toner, such as a liquid toner that includes a dispersion of colorant particles in an organic liquid, to create a toned image; and (d) transferring the toned image to a substrate.

In a fourth aspect, the invention features a charge transport material having the general formula above.

The invention provides suitable charge transport materials for
15 organophotoreceptors featuring a combination of good mechanical and electrostatic properties. These photoreceptors can be used successfully with liquid toners to produce high quality images. The high quality of the imaging system can be maintained after repeated cycling.

Other features and advantages of the invention will be apparent from the
20 following description of the particular embodiments thereof, and from the claims.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

An organophotoreceptor as described herein has an electrically conductive substrate and a photoconductive element including a charge generating compound and a
25 charge transport material having two aromatic hydrazone groups, each independently bonded to an arylamine group through a linking group having a hydrazone group. These charge transport materials have desirable properties as evidenced by their performance in organophotoreceptors for electrophotography. In particular, the charge transport materials of this invention have high charge carrier mobilities and good compatibility
30 with various binder materials, and possess excellent electrophotographic properties. The organophotoreceptors according to this invention generally have a high photosensitivity,

a low residual potential, and a high stability with respect to cycle testing, crystallization, and organophotoreceptor bending and stretching. The organophotoreceptors are particularly useful in laser printers and the like as well as fax machines, photocopiers, scanners and other electronic devices based on electrophotography. The use of these charge transport materials is described in more detail below in the context of laser printer use, although their application in other devices operating by electrophotography can be generalized from the discussion below.

To produce high quality images, particularly after multiple cycles, it is desirable for the charge transport materials to form a homogeneous solution with the polymeric binder and remain approximately homogeneously distributed through the organophotoreceptor material during the cycling of the material. In addition, it is desirable to increase the amount of charge that the charge transport material can accept (indicated by a parameter known as the acceptance voltage or " V_{acc} "), and to reduce retention of that charge upon discharge (indicated by a parameter known as the discharge voltage or " V_{dis} ").

The charge transport materials can be classified as a charge transport compound or an electron transport compound. There are many charge transport compounds and electron transport compounds known in the art for electrophotography. Non-limiting examples of charge transport compounds include, for example, pyrazoline derivatives, fluorene derivatives, oxadiazole derivatives, stilbene derivatives, enamine derivatives, enamine stilbene derivatives, hydrazone derivatives, carbazole hydrazone derivatives, (N,N-disubstituted)arylamines such as triaryl amines, polyvinyl carbazole, polyvinyl pyrene, polyacenaphthylene, or multi-hydrazone compounds comprising at least two hydrazone groups and at least two groups selected from the group consisting of (N,N-disubstituted)arylamine such as triphenylamine and heterocycles such as carbazole, julolidine, phenothiazine, phenazine, phenoxazine, phenoxathiin, thiazole, oxazole, isoxazole, dibenzo(1,4)dioxin, thianthrene, imidazole, benzothiazole, benzotriazole, benzoxazole, benzimidazole, quinoline, isoquinoline, quinoxaline, indole, indazole, pyrrole, purine, pyridine, pyridazine, pyrimidine, pyrazine, triazole, oxadiazole, tetrazole, thiadiazole, benzisoxazole, benzisothiazole, dibenzofuran, dibenzothiophene, thiophene, thianaphthene, quinazoline, or cinnoline.

Non-limiting examples of electron transport compounds include, for example, bromoaniline, tetracyanoethylene, tetracyanoquinodimethane, 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, 2,4,5,7-tetranitroxanthone, 2,4,8-trinitrothioxanthone, 2,6,8-trinitro-indeno[1,2-b]thiophene-4-one, and 1,3,7-trinitrodibenzo thiophene-5,5-dioxide, (2,3-diphenyl-1-indenylidene)malononitrile, 4H-thiopyran-1,1-dioxide and its derivatives such as 4-dicyanomethylene-2,6-diphenyl-4H-thiopyran-1,1-dioxide, 4-dicyanomethylene-2,6-di-m-tolyl-4H-thiopyran-1,1-dioxide, and unsymmetrically substituted 2,6-diaryl-4H-thiopyran-1,1-dioxide such as 4H-1,1-dioxo-2-(p-isopropylphenyl)-6-phenyl-4-(dicyanomethylidene)thiopyran and 4H-1,1-dioxo-2-(p-isopropylphenyl)-6-(2-thienyl)-4-(dicyanomethylidene)thiopyran, derivatives of phospho-2,5-cyclohexadiene, alkoxycarbonyl-9-fluorenylidene)malononitrile derivatives such as (4-n-butoxycarbonyl-9-fluorenylidene)malononitrile, (4-phenethoxycarbonyl-9-fluorenylidene)malononitrile, (4-carbitoxy-9-fluorenylidene)malononitrile, and diethyl(4-n-butoxycarbonyl-2,7-dinitro-9-fluorenylidene)malonate, anthraquinodimethane derivatives such as 11,11,12,12-tetracyano-2-alkylanthraquinodimethane and 11,11-dicyano-12,12-bis(ethoxycarbonyl)anthraquinodimethane, anthrone derivatives such as 1-chloro-10-[bis(ethoxycarbonyl)methylene]anthrone, 1,8-dichloro-10-[bis(ethoxycarbonyl)methylene]anthrone, 1,8-dihydroxy-10-[bis(ethoxycarbonyl)methylene]anthrone, and 1-cyano-10-[bis(ethoxycarbonyl)methylene]anthrone, 7-nitro-2-aza-9-fluorenylidene-malononitrile, diphenoquinone derivatives, benzoquinone derivatives, naphthoquinone derivatives, quinine derivatives, tetracyanoethylenecyanoethylene, 2,4,8-trinitro thioxanthone, dinitrobenzene derivatives, dinitroanthracene derivatives, dinitroacridine derivatives, nitroanthraquinone derivatives, dinitroanthraquinone derivatives, succinic anhydride, maleic anhydride, dibromo maleic anhydride, pyrene derivatives, carbazole derivatives, hydrazone derivatives, N,N-dialkylaniline derivatives, diphenylamine derivatives, triphenylamine derivatives, triphenylmethane derivatives, tetracyano quinodimethane, 2,4,5,7-tetranitro-9-fluorenone, 2,4,7-trinitro-9-dicyanomethylene fluorenone, 2,4,5,7-tetranitroxanthone derivatives, 2,4,8-trinitrothioxanthone derivatives, 1,4,5,8-naphthalene bis-dicarboximide derivatives as described in U.S. Patent Nos. 5,232,800, 4,468,444, and 4,442,193 and phenylazoquinolide derivatives as described in U.S. Patent No. 6,472,514. In some

embodiments of interest, the electron transport compound comprises an (alkoxycarbonyl-9-fluorenylidene)malononitrile derivative, such as (4-n-butoxycarbonyl-9-fluorenylidene)malononitrile, and 1,4,5,8-naphthalene bis-dicarboximide derivatives.

Although there are many charge transport materials available, there is a need for other charge transport materials to meet the various requirements of particular electrophotography applications.

In electrophotography applications, a charge-generating compound within an organophotoreceptor absorbs light to form electron-hole pairs. These electrons and holes can be transported over an appropriate time frame under a large electric field to discharge locally a surface charge that is generating the field. The discharge of the field at a particular location results in a surface charge pattern that essentially matches the pattern drawn with the light. This charge pattern then can be used to guide toner deposition. The charge transport materials described herein are especially effective at transporting charge, and in particular holes from the electron-hole pairs formed by the charge generating compound. In some embodiments, a specific electron transport compound or charge transport compound can also be used along with the charge transport material of this invention.

The layer or layers of materials containing the charge generating compound and the charge transport materials are within an organophotoreceptor. To print a two dimensional image using the organophotoreceptor, the organophotoreceptor has a two dimensional surface for forming at least a portion of the image. The imaging process then continues by cycling the organophotoreceptor to complete the formation of the entire image and/or for the processing of subsequent images.

The organophotoreceptor may be provided in the form of a plate, a flexible belt, a disk, a rigid drum, a sheet around a rigid or compliant drum, or the like. The charge transport material can be in the same layer as the charge generating compound and/or in a different layer from the charge generating compound. Additional layers can be used also, as described further below.

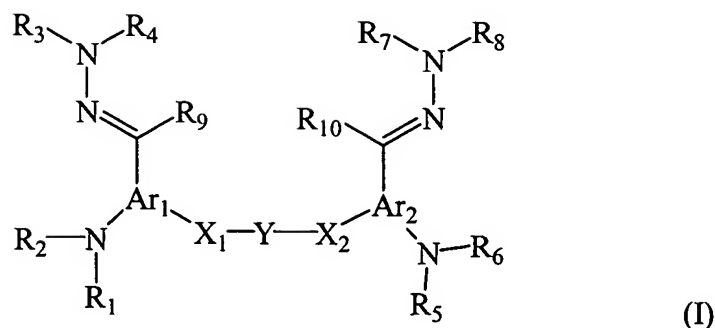
In some embodiments, the organophotoreceptor material comprises, for example: (a) a charge transport layer comprising the charge transport material and a polymeric binder; (b) a charge generating layer comprising the charge generating compound and a

polymeric binder; and (c) the electrically conductive substrate. The charge transport layer may be intermediate between the charge generating layer and the electrically conductive substrate. Alternatively, the charge generating layer may be intermediate between the charge transport layer and the electrically conductive substrate. In further
5 embodiments, the organophotoreceptor material has a single layer with both a charge transport material and a charge generating compound within a polymeric binder.

The organophotoreceptors can be incorporated into an electrophotographic imaging apparatus, such as laser printers. In these devices, an image is formed from physical embodiments and converted to a light image that is scanned onto the
10 organophotoreceptor to form a surface latent image. The surface latent image can be used to attract toner onto the surface of the organophotoreceptor, in which the toner image is the same or the negative of the light image projected onto the organophotoreceptor. The toner can be a liquid toner or a dry toner. The toner is subsequently transferred, from the surface of the organophotoreceptor, to a receiving
15 surface, such as a sheet of paper. After the transfer of the toner, the surface is discharged, and the material is ready to cycle again. The imaging apparatus can further comprise, for example, a plurality of support rollers for transporting a paper receiving medium and/or for movement of the photoreceptor, a light imaging component with suitable optics to form the light image, a light source, such as a laser, a toner source and delivery system
20 and an appropriate control system.

An electrophotographic imaging process generally can comprise (a) applying an electrical charge to a surface of the above-described organophotoreceptor; (b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of charged and uncharged areas on the surface;
25 (c) exposing the surface with a toner, such as a liquid toner that includes a dispersion of colorant particles in an organic liquid to create a toner image, to attract toner to the charged or discharged regions of the organophotoreceptor; and (d) transferring the toner image to a substrate.

As described herein, an organophotoreceptor comprises a charge transport
30 material having the formula:



where R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 are, each independently, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group;

R_9 and R_{10} are, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group;

Ar_1 and Ar_2 are, each independently, an aromatic group;

Y comprises an arylamine group, such as a carbazole group, a julolidine group, and an (N,N-disubstituted)arylamine group; and

X_1 and X_2 are, each independently, linking groups, such as a $-(CH_2)_m-N(R_{11})-N=C(R_{12})-$ group, where R_{11} and R_{12} are, each independently, hydrogen, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group, m is an integer between 1 and 30, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, or a SiR_eR_f where R_a , R_b , R_c , R_d , R_e , and R_f are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, an alkyl group, an alkoxy group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group.

A heterocyclic group includes any monocyclic or polycyclic (e.g., bicyclic, tricyclic, etc.) ring compound having at least a heteroatom (e.g., O, S, N, P, B, Si, etc.) in the ring.

An aromatic group can be any conjugated ring system containing $4n + 2$ pi-electrons. There are many criteria available for determining aromaticity. A widely employed criterion for the quantitative assessment of aromaticity is the resonance energy. Specifically, an aromatic group has a resonance energy. In some embodiments, the resonance energy of the aromatic group is at least 10 KJ/mol. In further embodiments, the resonance energy of the aromatic group is greater than 0.1 KJ/mol. Aromatic groups may

be classified as an aromatic heterocyclic group which contains at least a heteroatom in the $4n + 2$ pi-electron ring, or as an aryl group which does not contain a heteroatom in the $4n + 2$ pi-electron ring. The aromatic group may comprise a combination of aromatic heterocyclic group and aryl group. Nonetheless, either the aromatic heterocyclic or the aryl group may have at least one heteroatom in a substituent attached to the $4n + 2$ pi-electron ring. Furthermore, either the aromatic heterocyclic or the aryl group may comprise a monocyclic or polycyclic (such as bicyclic, tricyclic, etc.) ring.

Non-limiting examples of the aromatic heterocyclic group are furanyl, thiophenyl, pyrrolyl, indolyl, carbazolyl, benzofuranyl, benzothiophenyl, dibenzofuranyl, dibenzothiophenyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, triazinyl, tetrazinyl, petazinyl, quinolinyl, isoquinolinyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, naphthyridinyl, acridinyl, phenanthridinyl, phenanthrolinyl, anthyridinyl, purinyl, pteridinyl, alloxazinyl, phenazinyl, phenothiazinyl, phenoxazinyl, phenoxathiinyl, dibenzo(1,4)dioxinyl, thianthrenyl, and a combination thereof. The aromatic heterocyclic group may also include any combination of the above aromatic heterocyclic groups bonded together either by a bond (as in bicarbazolyl) or by a linking group (as in 1,6 di(10H-10-phenothiazinyl)hexane). The linking group may include an aliphatic group, an aromatic group, a heterocyclic group, or a combination thereof. Furthermore, either an aliphatic group or an aromatic group within a linking group may comprise at least one heteroatom such as O, S, Si, and N.

Non-limiting examples of the aryl group are phenyl, naphthyl, benzyl, or tolanyl group, sexiphenylene, phenanthrenyl, anthracenyl, coronenyl, and tolanylphenyl. The aryl group may also include any combination of the above aryl groups bonded together either by a bond (as in biphenyl group) or a linking group (as in stilbenyl, diphenyl sulfone, an arylamine group). The linking group may include an aliphatic group, an aromatic group, a heterocyclic group, or a combination thereof. Furthermore, either an aliphatic group or an aromatic group within a linking group may comprise at least one heteroatom such as O, S, Si, and N.

Substitution is liberally allowed on the chemical groups to affect various physical effects on the properties of the compounds, such as mobility, sensitivity, solubility, stability, and the like, as is known generally in the art. In the description of chemical

substituents, there are certain practices common to the art that are reflected in the use of language. The term group indicates that the generically recited chemical entity (e.g., alkyl group, phenyl group, aromatic group, arylamine group, julolidine group, carbazole group, (N,N-disubstituted)arylamine group, etc.) may have any substituent thereon which is consistent with the bond structure of that group. For example, where the term 'alkyl group' is used, that term would not only include unsubstituted linear, branched and cyclic alkyls, such as methyl, ethyl, isopropyl, tert-butyl, cyclohexyl, dodecyl and the like, but also substituents having heteroatom, such as 3-ethoxylpropyl, 4-(N,N-diethylamino)butyl, 3-hydroxypentyl, 2-thiolhexyl, 1,2,3-tribromopropyl, and the like, and aromatic group, such as phenyl, naphthyl, carbazolyl, pyrrole, and the like. However, as is consistent with such nomenclature, no substitution would be included within the term that would alter the fundamental bond structure of the underlying group. For example, where a phenyl group is recited, substitution such as 2- or 4-aminophenyl, 2- or 4-(N,N-disubstituted)aminophenyl, 2,4-dihydroxyphenyl, 2,4,6-trithiophenyl, 2,4,6-trimethoxyphenyl and the like would be acceptable within the terminology, while substitution of 1,1,2,2,3,3-hexamethylphenyl would not be acceptable as that substitution would require the ring bond structure of the phenyl group to be altered to a non-aromatic form. Similarly, when referring to arylamine group, the compound or substituent cited includes any substitution that does not substantively alter the chemical nature of the arylamine group in the formula. Where the term moiety is used, such as alkyl moiety or phenyl moiety, that terminology indicates that the chemical material is not substituted. Where the term alkyl moiety is used, that term represents only an unsubstituted alkyl hydrocarbon group, whether branched, straight chain, or cyclic.

Organophotoreceptors

The organophotoreceptor may be, for example, in the form of a plate, a sheet, a flexible belt, a disk, a rigid drum, or a sheet around a rigid or compliant drum, with flexible belts and rigid drums generally being used in commercial embodiments. The organophotoreceptor may comprise, for example, an electrically conductive substrate and on the electrically conductive substrate a photoconductive element in the form of one or more layers. The photoconductive element can comprise both a charge transport material

and a charge generating compound in a polymeric binder, which may or may not be in the same layer, as well as a second charge transport material such as a charge transport compound or an electron transport compound in some embodiments. For example, the charge transport material and the charge generating compound can be in a single layer.

5 In other embodiments, however, the photoconductive element comprises a bilayer construction featuring a charge generating layer and a separate charge transport layer. The charge generating layer may be located intermediate between the electrically conductive substrate and the charge transport layer. Alternatively, the photoconductive element may have a structure in which the charge transport layer is intermediate between
10 the electrically conductive substrate and the charge generating layer.

The electrically conductive substrate may be flexible, for example in the form of a flexible web or a belt, or inflexible, for example in the form of a drum. A drum can have a hollow cylindrical structure that provides for attachment of the drum to a drive that rotates the drum during the imaging process. Typically, a flexible electrically conductive
15 substrate comprises an electrically insulating substrate and a thin layer of electrically conductive material onto which the photoconductive material is applied.

The electrically insulating substrate may be paper or a film forming polymer such as polyester (e.g., polyethylene terephthalate or polyethylene naphthalate), polyimide, polysulfone, polypropylene, nylon, polyester, polycarbonate, polyvinyl resin, polyvinyl
20 fluoride, polystyrene and the like. Specific examples of polymers for supporting substrates included, for example, polyethersulfone (STABAR™ S-100, available from ICI), polyvinyl fluoride (Tedlar®, available from E.I. DuPont de Nemours & Company), polybisphenol-A polycarbonate (MAKROFOL™, available from Mobay Chemical Company) and amorphous polyethylene terephthalate (MELINAR™, available from ICI
25 Americas, Inc.). The electrically conductive materials may be graphite, dispersed carbon black, iodine, conductive polymers such as polypyrroles and Calgon® conductive polymer 261 (commercially available from Calgon Corporation, Inc., Pittsburgh, Pa.), metals such as aluminum, titanium, chromium, brass, gold, copper, palladium, nickel, or stainless steel, or metal oxide such as tin oxide or indium oxide. In embodiments of
30 particular interest, the electrically conductive material is aluminum. Generally, the photoconductor substrate has a thickness adequate to provide the required mechanical

stability. For example, flexible web substrates generally have a thickness from about 0.01 to about 1 mm, while drum substrates generally have a thickness from about 0.5 mm to about 2 mm.

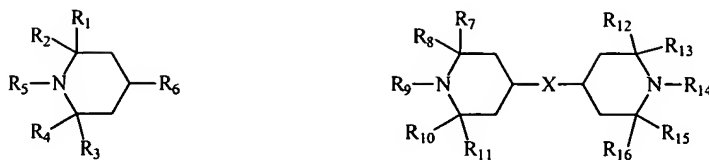
The charge generating compound is a material that is capable of absorbing light to generate charge carriers (such as a dye or pigment). Non-limiting examples of suitable charge generating compounds include, for example, metal-free phthalocyanines (e.g., ELA 8034 metal-free phthalocyanine available from H.W. Sands, Inc. or Sanyo Color Works, Ltd., CGM-X01), metal phthalocyanines such as titanium phthalocyanine, copper phthalocyanine, oxytitanium phthalocyanine (also referred to as titanyl oxyphthalocyanine, and including any crystalline phase or mixtures of crystalline phases that can act as a charge generating compound), hydroxygallium phthalocyanine, squarylium dyes and pigments, hydroxy-substituted squarylium pigments, perylimides, polynuclear quinones available from Allied Chemical Corporation under the trade name INDOFAST™ Double Scarlet, INDOFAST™ Violet Lake B, INDOFAST™ Brilliant Scarlet and INDOFAST™ Orange, quinacridones available from DuPont under the trade name MONASTRAL™ Red, MONASTRAL™ Violet and MONASTRAL™ Red Y, naphthalene 1,4,5,8-tetracarboxylic acid derived pigments including the perinones, tetrabenzoporphyrins and tetranaphthaloporphyrins, indigo- and thioindigo dyes, benzothioxanthene-derivatives, perylene 3,4,9,10-tetracarboxylic acid derived pigments, polyazo-pigments including bisazo-, trisazo- and tetrakisazo-pigments, polymethine dyes, dyes containing quinazoline groups, tertiary amines, amorphous selenium, selenium alloys such as selenium-tellurium, selenium-tellurium-arsenic and selenium-arsenic, cadmium sulphoselenide, cadmium selenide, cadmium sulphide, and mixtures thereof. For some embodiments, the charge generating compound comprises oxytitanium phthalocyanine (e.g., any phase thereof), hydroxygallium phthalocyanine or a combination thereof.

The photoconductive layer of this invention may optionally contain a second charge transport material which may be a charge transport compound, an electron transport compound, or a combination of both. Generally, any charge transport compound or electron transport compound known in the art can be used as the second charge transport material.

An electron transport compound and a UV light stabilizer can have a synergistic relationship for providing desired electron flow within the photoconductor. The presence of the UV light stabilizers alters the electron transport properties of the electron transport compounds to improve the electron transporting properties of the composite. UV light stabilizers can be ultraviolet light absorbers or ultraviolet light inhibitors that trap free radicals.

UV light absorbers can absorb ultraviolet radiation and dissipate it as heat. UV light inhibitors are thought to trap free radicals generated by the ultraviolet light and after trapping of the free radicals, subsequently to regenerate active stabilizer moieties with energy dissipation. In view of the synergistic relationship of the UV stabilizers with electron transport compounds, the particular advantages of the UV stabilizers may not be their UV stabilizing abilities, although the UV stabilizing ability may be further advantageous in reducing degradation of the organophotoreceptor over time. The improved synergistic performance of organophotoreceptors with layers comprising both an electron transport compound and a UV stabilizer are described further in copending U.S. Patent Application Serial Number 10/425,333 filed on April 28, 2003 to Zhu, entitled "Organophotoreceptor With A Light Stabilizer," incorporated herein by reference.

Non-limiting examples of suitable light stabilizer include, for example, hindered trialkylamines such as Tinuvin 144 and Tinuvin 292 (from Ciba Specialty Chemicals, Terrytown, NY), hindered alkoxydialkylamines such as Tinuvin 123 (from Ciba Specialty Chemicals), benzotriazoles such as Tinuvin 328, Tinuvin 900 and Tinuvin 928 (from Ciba Specialty Chemicals), benzophenones such as Sanduvor 3041 (from Clariant Corp., Charlotte, N.C.), nickel compounds such as Arbestab (from Robinson Brothers Ltd, West Midlands, Great Britain), salicylates, cyanocinnamates, benzylidene malonates, benzoates, oxanilides such as Sanduvor VSU (from Clariant Corp., Charlotte, N.C.), triazines such as Cyagard UV-1164 (from Cytec Industries Inc., N.J.), polymeric sterically hindered amines such as Luchem (from Atochem North America, Buffalo, NY). In some embodiments, the light stabilizer is selected from the group consisting of hindered trialkylamines having the following formula:



where $R_1, R_2, R_3, R_4, R_6, R_7, R_8, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15}$ are, each independently, hydrogen, alkyl group, or ester, or ether group; and R_5, R_9 , and R_{14} are, each independently, alkyl group; and X is a linking group selected from the group consisting of $-O-CO-(CH_2)_m-CO-O-$ where m is between 2 to 20.

The binder generally is capable of dispersing or dissolving the charge transport material (in the case of the charge transport layer or a single layer construction), the charge generating compound (in the case of the charge generating layer or a single layer construction) and/or an electron transport compound for appropriate embodiments.

Examples of suitable binders for both the charge generating layer and charge transport layer generally include, for example, polystyrene-co-butadiene, polystyrene-co-acrylonitrile, modified acrylic polymers, polyvinyl acetate, styrene-alkyd resins, soya-alkyl resins, polyvinylchloride, polyvinylidene chloride, polyacrylonitrile, polycarbonates, polyacrylic acid, polyacrylates, polymethacrylates, styrene polymers, polyvinyl butyral, alkyd resins, polyamides, polyurethanes, polyesters, polysulfones, polyethers, polyketones, phenoxy resins, epoxy resins, silicone resins, polysiloxanes, poly(hydroxyether) resins, polyhydroxystyrene resins, novolak, poly(phenylglycidyl ether)-co-dicyclopentadiene, copolymers of monomers used in the above-mentioned polymers, and combinations thereof. Specific suitable binders include, for example, polyvinyl butyral, polycarbonate, and polyester. Non-limiting examples of polyvinyl butyral include BX-1 and BX-5 from Sekisui Chemical Co. Ltd., Japan. Non-limiting examples of suitable polycarbonate include polycarbonate A which is derived from bisphenol-A (e.g. Iupilon-A from Mitsubishi Engineering Plastics, or Lexan 145 from General Electric); polycarbonate Z which is derived from cyclohexylidene bisphenol (e.g. Iupilon-Z from Mitsubishi Engineering Plastics Corp, White Plain, New York); and polycarbonate C which is derived from methylbisphenol A (from Mitsubishi Chemical Corporation). Non-limiting examples of suitable polyester binders include ortho-polyethylene terephthalate (e.g. OPET TR-4 from Kanebo Ltd., Yamaguchi, Japan).

Suitable optional additives for any one or more of the layers include, for example, antioxidants, coupling agents, dispersing agents, curing agents, surfactants, and combinations thereof.

The photoconductive element overall typically has a thickness from about 10
5 microns to about 45 microns. In the dual layer embodiments having a separate charge generating layer and a separate charge transport layer, charge generation layer generally has a thickness from about 0.5 microns to about 2 microns, and the charge transport layer has a thickness from about 5 microns to about 35 microns. In embodiments in which the charge transport material and the charge generating compound are in the same layer, the
10 layer with the charge generating compound and the charge transport composition generally has a thickness from about 7 microns to about 30 microns. In embodiments with a distinct electron transport layer, the electron transport layer has an average thickness from about 0.5 microns to about 10 microns and in further embodiments from about 1 micron to about 3 microns. In general, an electron transport overcoat layer can
15 increase mechanical abrasion resistance, increases resistance to carrier liquid and atmospheric moisture, and decreases degradation of the photoreceptor by corona gases. A person of ordinary skill in the art will recognize that additional ranges of thickness within the explicit ranges above are contemplated and are within the present disclosure.

Generally, for the organophotoreceptors described herein, the charge generation
20 compound is in an amount from about 0.5 to about 25 weight percent, in further embodiments in an amount from about 1 to about 15 weight percent, and in other embodiments in an amount from about 2 to about 10 weight percent, based on the weight of the photoconductive layer. The charge transport material is in an amount from about 10 to about 80 weight percent, based on the weight of the photoconductive layer, in
25 further embodiments in an amount from about 35 to about 60 weight percent, and in other embodiments from about 45 to about 55 weight percent, based on the weight of the photoconductive layer. The optional second charge transport material, when present, can be in an amount of at least about 2 weight percent, in other embodiments from about 2.5 to about 25 weight percent, based on the weight of the photoconductive layer, and in
30 further embodiments in an amount from about 4 to about 20 weight percent, based on the weight of the photoconductive layer. The binder is in an amount from about 15 to about

80 weight percent, based on the weight of the photoconductive layer, and in further embodiments in an amount from about 20 to about 75 weight percent, based on the weight of the photoconductive layer. A person of ordinary skill in the art will recognize that additional ranges within the explicit ranges of compositions are contemplated and are within the present disclosure.

For the dual layer embodiments with a separate charge generating layer and a charge transport layer, the charge generation layer generally comprises a binder in an amount from about 10 to about 90 weight percent, in further embodiments from about 15 to about 80 weight percent and in some embodiments in an amount from about 20 to about 75 weight percent, based on the weight of the charge generation layer. The optional charge transport material in the charge generating layer, if present, generally can be in an amount of at least about 2.5 weight percent, in further embodiments from about 4 to about 30 weight percent and in other embodiments in an amount from about 10 to about 25 weight percent, based on the weight of the charge generating layer. The charge transport layer generally comprises a binder in an amount from about 20 weight percent to about 70 weight percent and in further embodiments in an amount from about 30 weight percent to about 50 weight percent. A person of ordinary skill in the art will recognize that additional ranges of binder concentrations for the dual layer embodiments within the explicit ranges above are contemplated and are within the present disclosure.

For the embodiments with a single layer having a charge generating compound and a charge transport material, the photoconductive layer generally comprises a binder, a charge transport material, and a charge generation compound. The charge generation compound can be in an amount from about 0.05 to about 25 weight percent and in further embodiment in an amount from about 2 to about 15 weight percent, based on the weight of the photoconductive layer. The charge transport material can be in an amount from about 10 to about 80 weight percent, in other embodiments from about 25 to about 65 weight percent, in additional embodiments from about 30 to about 60 weight percent and in further embodiments in an amount from about 35 to about 55 weight percent, based on the weight of the photoconductive layer, with the remainder of the photoconductive layer comprising the binder, and optionally additives, such as any conventional additives. A single layer with a charge transport composition and a charge generating compound

generally comprises a binder in an amount from about 10 weight percent to about 75 weight percent, in other embodiments from about 20 weight percent to about 60 weight percent, and in further embodiments from about 25 weight percent to about 50 weight percent. Optionally, the layer with the charge generating compound and the charge transport material may comprise a second charge transport material. The optional second charge transport material, if present, generally can be in an amount of at least about 2.5 weight percent, in further embodiments from about 4 to about 30 weight percent and in other embodiments in an amount from about 10 to about 25 weight percent, based on the weight of the photoconductive layer. A person of ordinary skill in the art will recognize that additional composition ranges within the explicit compositions ranges for the layers above are contemplated and are within the present disclosure.

In general, any layer with an electron transport layer can advantageously further include a UV light stabilizer. In particular, the electron transport layer generally can comprise an electron transport compound, a binder, and an optional UV light stabilizer. An overcoat layer comprising an electron transport compound is described further in copending U.S. Patent Application Serial No. 10/396,536 to Zhu et al. entitled, "Organophotoreceptor With An Electron Transport Layer," incorporated herein by reference. For example, an electron transport compound as described above may be used in the release layer of the photoconductors described herein. The electron transport compound in an electron transport layer can be in an amount from about 10 to about 50 weight percent, and in other embodiments in an amount from about 20 to about 40 weight percent, based on the weight of the electron transport layer. A person of ordinary skill in the art will recognize that additional ranges of compositions within the explicit ranges are contemplated and are within the present disclosure.

The UV light stabilizer, if present, in any one or more appropriate layers of the photoconductor generally is in an amount from about 0.5 to about 25 weight percent and in some embodiments in an amount from about 1 to about 10 weight percent, based on the weight of the particular layer. A person of ordinary skill in the art will recognize that additional ranges of compositions within the explicit ranges are contemplated and are within the present disclosure.

For example, the photoconductive layer may be formed by dispersing or dissolving the components, such as one or more of a charge generating compound, the charge transport material of this invention, a second charge transport material such as a charge transport compound or an electron transport compound, a UV light stabilizer, and
5 a polymeric binder in organic solvent, coating the dispersion and/or solution on the respective underlying layer and drying the coating. In particular, the components can be dispersed by high shear homogenization, ball-milling, attritor milling, high energy bead (sand) milling or other size reduction processes or mixing means known in the art for effecting particle size reduction in forming a dispersion.

10 The photoreceptor may optionally have one or more additional layers as well. An additional layer can be, for example, a sub-layer or an overcoat layer, such as a barrier layer, a release layer, a protective layer, or an adhesive layer. A release layer or a protective layer may form the uppermost layer of the photoconductor element. A barrier layer may be sandwiched between the release layer and the photoconductive element or
15 used to overcoat the photoconductive element. The barrier layer provides protection from abrasion to the underlayers. An adhesive layer locates and improves the adhesion between a photoconductive element, a barrier layer and a release layer, or any combination thereof. A sub-layer is a charge blocking layer and locates between the electrically conductive substrate and the photoconductive element. The sub-layer may
20 also improve the adhesion between the electrically conductive substrate and the photoconductive element.

Suitable barrier layers include, for example, coatings such as crosslinkable siloxanol-colloidal silica coating and hydroxylated silsesquioxane-colloidal silica coating, and organic binders such as polyvinyl alcohol, methyl vinyl ether/maleic anhydride
25 copolymer, casein, polyvinyl pyrrolidone, polyacrylic acid, gelatin, starch, polyurethanes, polyimides, polyesters, polyamides, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polycarbonates, polyvinyl butyral, polyvinyl acetoacetal, polyvinyl formal, polyacrylonitrile, polymethyl methacrylate, polyacrylates, polyvinyl carbazoles, copolymers of monomers used in the above-mentioned polymers, vinyl chloride/vinyl
30 acetate/vinyl alcohol terpolymers, vinyl chloride/vinyl acetate/maleic acid terpolymers, ethylene/vinyl acetate copolymers, vinyl chloride/vinylidene chloride copolymers,

cellulose polymers, and mixtures thereof. The above barrier layer polymers optionally may contain small inorganic particles such as fumed silica, silica, titania, alumina, zirconia, or a combination thereof. Barrier layers are described further in U.S. Patent 6,001,522 to Woo et al., entitled "Barrier Layer For Photoconductor Elements
 5 Comprising An Organic Polymer And Silica," incorporated herein by reference. The release layer topcoat may comprise any release layer composition known in the art. In some embodiments, the release layer is a fluorinated polymer, siloxane polymer, fluorosilicone polymer, silane, polyethylene, polypropylene, polyacrylate, or a combination thereof. The release layers can comprise crosslinked polymers.

10 The release layer may comprise, for example, any release layer composition known in the art. In some embodiments, the release layer comprises a fluorinated polymer, siloxane polymer, fluorosilicone polymer, polysilane, polyethylene, polypropylene, polyacrylate, poly(methyl methacrylate-co-methacrylic acid), urethane resins, urethane-epoxy resins, acrylated-urethane resins, urethane-acrylic resins, or a
 15 combination thereof. In further embodiments, the release layers comprise crosslinked polymers.

The protective layer can protect the organophotoreceptor from chemical and mechanical degradation. The protective layer may comprise any protective layer composition known in the art. In some embodiments, the protective layer is a fluorinated
 20 polymer, siloxane polymer, fluorosilicone polymer, polysilane, polyethylene, polypropylene, polyacrylate, poly(methyl methacrylate-co-methacrylic acid), urethane resins, urethane-epoxy resins, acrylated-urethane resins, urethane-acrylic resins, or a combination thereof. In some embodiments of particular interest, the release layers are crosslinked polymers.

25 An overcoat layer may comprise an electron transport compound as described further in copending U.S. Patent Application Serial No. 10/396,536, filed on March 25, 2003 to Zhu et al. entitled, "Organoreceptor With An Electron Transport Layer," incorporated herein by reference. For example, an electron transport compound, as described above, may be used in the release layer of this invention. The electron
 30 transport compound in the overcoat layer can be in an amount from about 2 to about 50 weight percent, and in other embodiments in an amount from about 10 to about 40 weight

percent, based on the weight of the release layer. A person of ordinary skill in the art will recognize that additional ranges of composition within the explicit ranges are contemplated and are within the present disclosure.

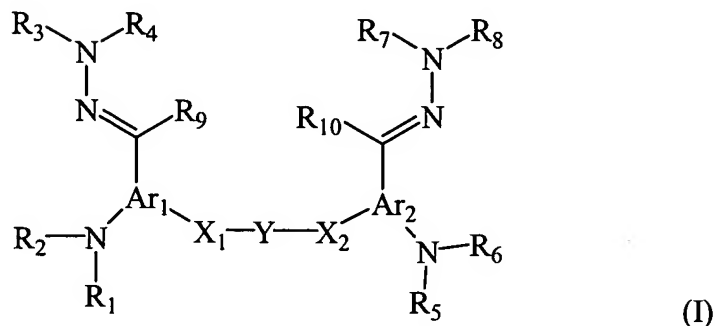
Generally, adhesive layers comprise a film forming polymer, such as polyester,
 5 polyvinylbutyral, polyvinylpyrrolidone, polyurethane, polymethyl methacrylate, poly(hydroxy amino ether) and the like. Barrier and adhesive layers are described further in U.S. Patent 6,180,305 to Ackley et al., entitled "Organic Photoreceptors for Liquid Electrophotography," incorporated herein by reference.

Sub-layers can comprise, for example, polyvinylbutyral, organosilanes,
 10 hydrolyzable silanes, epoxy resins, polyesters, polyamides, polyurethanes, cellulose and the like. In some embodiments, the sub-layer has a dry thickness between about 20 Angstroms and about 20,000 Angstroms. Sublayers containing metal oxide conductive particles can be between about 1 and about 25 microns thick. A person of ordinary skill in the art will recognize that additional ranges of compositions and thickness within the
 15 explicit ranges are contemplated and are within the present disclosure.

The charge transport materials as described herein, and photoreceptors including these compounds, are suitable for use in an imaging process with either dry or liquid toner development. For example, any dry toners and liquid toners known in the art may be used in the process and the apparatus of this invention. Liquid toner development can
 20 be desirable because it offers the advantages of providing higher resolution images and requiring lower energy for image fixing compared to dry toners. Examples of suitable liquid toners are known in the art. Liquid toners generally comprise toner particles dispersed in a carrier liquid. The toner particles can comprise a colorant/pigment, a resin binder, and/or a charge director. In some embodiments of liquid toner, a resin to pigment
 25 ratio can be from 1:1 to 10:1, and in other embodiments, from 4:1 to 8:1. Liquid toners are described further in Published U.S. Patent Applications 2002/0128349, entitled "Liquid Inks Comprising A Stable Organosol," and 2002/0086916, entitled "Liquid Inks Comprising Treated Colorant Particles," and U.S. Patent No. 6,649,316, entitled "Phase Change Developer For Liquid Electrophotography," all three of which are incorporated
 30 herein by reference.

Charge Transport Material

As described herein, an organophotoreceptor comprises a charge transport material having the formula



where R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 are, each independently, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group;

R_9 and R_{10} are, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group;

Ar_1 and Ar_2 are, each independently, an aromatic group;

Y comprises an arylamine group, such as a carbazole group, a julolidine group, and an (N,N-disubstituted)arylamine group; and

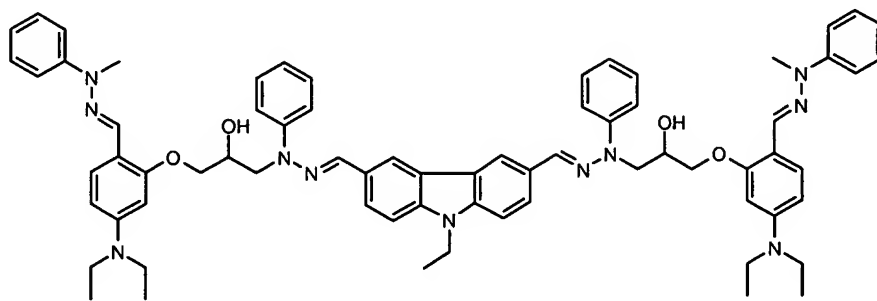
X_1 and X_2 are, each independently, linking groups, such as a $-(CH_2)_m-N(R_{11})-N=C(R_{12})-$ group, where R_{11} and R_{12} are, each independently, hydrogen, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, or a heterocyclic group, m is an integer between 1 and 30, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, a heterocyclic group, an aromatic group, an NR_a group, a CR_b group, a CR_cR_d group, or a SiR_eR_f where R_a , R_b , R_c , R_d , R_e , and R_f are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, an alkyl group, an alkoxy group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as benzo ring, cycloalkyl rings, and heterocyclic rings.

With respect to Formula (I), substitution is liberally allowed, especially on Y , X_1 , X_2 , Ar_1 , and Ar_2 . Variation of the substituents, such as an aromatic group, an alkyl group, a heterocyclic group, and a ring group such as a benzo group, on Y , X_1 , X_2 , Ar_1 , and Ar_2 can result in various physical effects on the properties of the compounds, such as mobility, solubility, compatibility, stability, spectral absorbance, dispersibility, and the

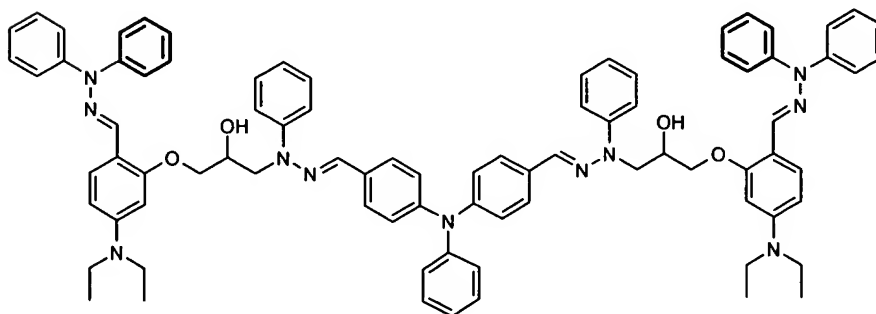
like, including, for example, substitutions known in the art to effect particular modifications.

The charge transport material of Formula (I) may be symmetrical or unsymmetrical. Thus, for example, X_1 and X_2 may be the same or different. Similarly, Ar_1 and Ar_2 may be the same or different; NR_1R_2 and NR_5R_6 may be the same or different; NR_3R_4 and NR_7R_8 may be the same or different; R_9 and R_{10} may be the same or different; or Y may be symmetrical or unsymmetrical. In addition, Formula (I) for the charge transport material is intended to cover isomers.

In some embodiments, the organophotoreceptors as described herein can comprise an improved charge transport material of Formula (I) where X_1 and X_2 are, each independently, a $-Q_1-CH_2-CH(Q_2H)-CH_2-N(R)-N=C(R')-$ group where Q_1 and Q_2 are, each independently, O, S or NR'' , where R, R', and R'' are, each independently, hydrogen, an alkyl group, an alkenyl group, an alkynyl group, or an aromatic group; Y is a carbazole group; and Ar_1 and Ar_2 are, each independently, a C_6H_3 group. In some further embodiments, Q_1 and Q_2 are, each independently, O. Specific, non-limiting examples of suitable charge transport materials within Formula (I) of the present invention have the following structures:



(1) and



(2).

Synthesis Of Charge Transport Materials

The synthesis of the charge transport materials of this invention can be prepared by the following multi-step synthetic procedures, although other suitable procedures can be used by a person of ordinary skill in the art based on the disclosure herein.

5

A First General Synthetic Procedure for Charge Transport Materials of Formula (I)

For some charge transport materials of Formula (I), the first step is the preparation of an arylamine compounds having two reactive ring groups and two aromatic hydrazone groups, such as 9-ethylcarbazole-3,6-dicarbaldehyde bis(N-2,3-epoxypropyl-N-phenyl)hydrazone and 4,4'-diformyltriphenylamino-bis(N-2,3-epoxy-propyl-N-phenylhydrazone). The reactive ring group can react with a reactive functional group such as hydroxyl, thiol, amino group, and carboxyl group. Non-limiting examples of suitable reactive ring group include epoxy group, thiiranyl group, or aziridino group. The preparations of such arylamine compounds have been disclosed in U.S. Patent Application Nos. 10/634,164, 10/772,068, and 10/749,178, all of which are incorporated herein by reference. The reactive ring groups have been disclosed in U.S. Patent Application Nos. 10/772,069, 10/789,077, and 10/789,184, all of which are incorporated herein by reference.

The second step is the preparation of an (N,N-disubstituted)hydrazone of an aromatic aldehyde or ketone having an (N,N-disubstituted)amino group and, on the aromatic ring, a reactive functional group that can react with the reactive ring group. Non-limiting examples of the functional group are hydroxyl, thiol, amino group, and carboxyl group. The (N,N-disubstituted)hydrazone can be prepared, for example, by the reaction of a corresponding aromatic aldehyde or ketone having a functional group, such as 4-diethylamino-2-hydroxybenzaldehyde, with a corresponding (N,N-disubstituted)hydrazine, such as N,N-diphenylhydrazine, in refluxing ethanol. The reaction can be catalyzed by an appropriate amount of concentrated acid, such as sulfuric acid and hydrochloric acid. The preparation of such (N,N-disubstituted)hydrazones of an aromatic aldehyde or ketone having an (N,N-disubstituted)amino group and, on the aromatic ring, a functional group has been disclosed in U.S. Patent Application No. 10/749,164, which is incorporated herein by reference.

The next step is the reactive-ring-opening reaction of an arylamine compound obtained in the first step with at least an (N,N-disubstituted)hydrazone obtained in the second step. If a symmetrical charge transport material of Formula (I) is desired, one part by mole of the arylamine compound may react with 2 parts by mole of the (N,N-disubstituted)hydrazone. The reaction can be catalyzed by an appropriate amount of concentrated acid, such as sulfuric acid and hydrochloric acid. If an unsymmetrical charge transport material of Formula (I) is desired, an unsymmetrical arylamine compound obtained in the first step may be used. Such unsymmetrical arylamine compounds having two reactive ring groups and two aromatic hydrazone groups have been disclosed in U.S. Patent Application Nos. 10/772,068 and 10/749,178, all of which are incorporated herein by reference. Alternatively, unsymmetrical charge transport materials of Formula (I) may be prepared by reacting an arylamine compound obtained in the first step sequentially with two (N,N-disubstituted)hydrazones obtained in the second step, either sequentially or simultaneously. The molar ratio of the three reactants may be 1:1:1. The reaction conditions can be selected to encourage the formation of the asymmetric compound, such as the sequential reaction with a greater than stoichiometric amount of an (N,N-disubstituted)hydrazone used in the first sequential reaction. To the extent that a mixture of symmetric and asymmetric compounds is formed, the different compounds can be separated from each other, for example, by conventional purification techniques, such as column chromatography, thin layer chromatography, and recrystallization.

An Alternative General Synthetic Procedure for Charge Transport Materials of Formula (I)

The first step is the preparation of an arylamine compound having two reactive functional groups such as hydroxyl, thiol, amino group, and carboxyl group. Such arylamine compounds may be prepared, for example, by the dicarbonylation, such as diformylation, of an arylamine compound, such as carbazole or triphenylamine, to form a dicarbonyl-arylamine compound, and followed by the reduction of the dicarbonyl-arylamine compound to the corresponding dihydroxy-arylamine compound by a reducing agent, such as hydrogen, metal, or metal hydrides. The preparation of the dicarbonyl-arylamine compounds, such as N-ethyl-3,6-diformylcarbazole and 4-(4-

formyldiphenylamino)benzaldehyde, have been disclosed in U.S. Patent Application Nos. 10/634,164, 10/772,068, and 10/749,178, all of which are incorporated herein by reference. The reduction of carbonyl compounds is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 193-239, which is incorporated herein by reference.

The second step is the preparation of a dihydrazone compound of an aromatic dialdehyde or diketone having an (N,N-disubstituted)amino group and a reactive ring group attached to one of two hydrazone groups. The dihydrazone compound can be prepared by the reacting an (N,N-disubstituted)aromatic amine having two aldehyde or ketone groups, such as 2-(1-piperidinyl)anthra-9,10-quinone (may be obtained from Aldrich), successively with an (N,N-disubstituted)hydrazine and an (N-substituted)hydrazine to form the corresponding dihydrazone compound having an (N,N-disubstituted)hydrazone group and an (N-substituted)hydrazone group. Then the NH nitrogen in the (N-substituted)hydrazone group may react with an organic halide containing one reactive ring group, such as an epoxy group, a thiiranyl group, or an aziridino group, to form the corresponding dihydrazone compound of an aromatic dialdehyde or diketone having an (N,N-disubstituted)amino group and a reactive ring group attached to one of two hydrazone groups. Non-limiting examples of suitable organic halide comprising an epoxy group for this invention are epihalohydrins, such as epichlorohydrin. The organic halide comprising an epoxy group can also be prepared by the epoxidation reaction of the corresponding alkene having a halide group. Such epoxidation reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 494-498, incorporated herein by reference. The alkene having a halide group can be prepared by the Wittig reaction between a suitable aldehyde or keto compound and a suitable Wittig reagent. The Wittig and related reactions are described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 69-77, incorporated herein by reference. The thiiranyl compound can be obtained by reacting the corresponding epoxy compound with ammonium thiocyanate in refluxing tetrahydrofuran (THF).

The (N,N-disubstituted)aromatic amine having two aldehyde or ketone groups may be prepared by Vilsmeier-Haack acylation by reacting the corresponding (N,N-

disubstituted)aromatic amine, such as triarylamine, diarylalkylamines or dialkylarylamines, or the corresponding (N,N-disubstituted)aromatic amine having one aldehyde or ketone group, such as 4-(dimethylamino)benzaldehyde, 4-diethylaminobenzaldehyde, 4-dimethylamino-1-naphthaldehyde, 4-(dibutylamino)-
 5 benzaldehyde, 4-(dimethylamino)benzophenone, 4-(diethylamino)benzophenone, 4-(Diphenylamino)benzaldehyde, with a mixture of phosphorus oxychloride (POCl₃) and a dialkylamide, such as N,N-dimethylformamide. The Vilsmeier-Haack acylation and related reactions are described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 380-393, incorporated herein by
 10 reference.

The next step is the reactive-ring-opening reaction of an arylamine compound obtained in the first step with at least a dihydrazone compound obtained in the second step. If a symmetrical charge transport material of Formula (I) is desired, one part by mole of the arylamine compound may react with 2 parts by mole of the dihydrazone
 15 compound. The reaction can be catalyzed by an appropriate amount of concentrated acid, such as sulfuric acid and hydrochloric acid. If an unsymmetrical charge transport material of Formula (I) is desired, an unsymmetrical arylamine compound obtained in the first step may be used. Alternatively, unsymmetrical charge transport materials of Formula (I) may be prepared by reacting an arylamine compound obtained in the first
 20 step with two different dihydrazone compounds obtained in the second step, either sequentially or simultaneously. The molar ratio of the three reactants may be 1:1:1. The reaction conditions can be selected to encourage the formation of the asymmetric compound, such as the sequential reaction with a greater than stoichiometric amount of a dihydrazone compound used in the first sequential reaction. To the extent that a mixture
 25 of symmetric and asymmetric compounds is formed, the different compounds can be separated from each other, for example, by conventional purification techniques, such as column chromatography, thin layer chromatography, and recrystallization.

The invention will now be described further by way of the following examples.

EXAMPLES

Example 1 - Synthesis And Characterization Charge Transport Materials

This example describes the synthesis and characterization of Compounds 1-2 in which the numbers refer to formula numbers above. The characterization involves chemical characterization of the compounds. The electrostatic characterization, such as mobility and ionization potential, of the materials formed with the compounds is presented in a subsequent example.

4-Diethylamino-2-hydroxybenzaldehyde N,N-diphenylhydrazone

A solution of N,N-diphenylhydrazine hydrochloride (79.5 g, 0.36 mol, from Aldrich, Milwaukee, WI) in ethanol (500 ml) was slowly added to a solution of 4-diethylamino-2-hydroxybenzaldehyde (58.0 g, 0.3 mol, from Aldrich, Milwaukee, WI) in ethanol (500 ml) in the presence of excess sodium carbonate. The reaction mixture was refluxed until 4-diethylamino-2-hydroxybenzaldehyde was completely reacted in about 30 minutes. The solvent (800 ml) was removed by evaporation. The residue obtained was extracted with ether and the ether extract was washed with water until the pH of the water reached 7. The organic layer was dried over anhydrous magnesium sulfate, treated with activated charcoal, and filtered. The ether solvent was evaporated. The residue was recrystallized from ethanol. Crystals were filtered off and washed with cold ethanol. The product was 4-diethylamino-2-hydroxybenzaldehyde N,N-diphenylhydrazone. The yield was 85 g (78.8 %). The melting point was found to be 95.5-96.5 °C (recrystallized from a mixture of 2-propanol and ether in a 10:1 ratio by volume). The ¹H-NMR spectrum (100 Mhz) of the product in CDCl₃ was characterized by the following chemical shifts (in ppm): 11.55 (s, 1H, OH); 7.55-6.95 (m, 11H, CH=N, Ph); 6.7 (d, *J*=8.6 Hz; 1H, 6-H of 1,2,4-subst. Ph); 6.23 (s, 1H, 3-H of 1,2,4-subst. Ph); 6.1 (d, *J*=8.6 Hz, 1H, 5-H of 1,2,4-subst. Ph); 3.3 (q, *J*=8.0 Hz, 4H, CH₂); 1.1 (t, *J*=8.0 Hz, 6H, CH₃). An elemental analysis yielded the following results in weight percent: C 76.68; H 7.75; N 11.45, which compared with calculated values for C₂₃H₂₅N₃O in weight percent of: C 76.85; H 7.01; N 11.69.

Preparation of 4-(diethylamino)salicylaldehyde N-methyl-N-phenylhydrazone

A mixture of 4-(diethylamino)salicylaldehyde (10 g, 52 mmol, obtained from Aldrich) dissolved in 80 ml of 2-propanol, and N-methyl-N-phenylhydrazine (6.8 ml, 63 mmol, obtained from Aldrich) was added to a 250 ml round bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction mixture was refluxed until 4-(diethylamino)salicylaldehyde completely reacted. After the termination of the reaction, the reaction mixture was cooled to room temperature. The crystals formed were filtered and washed repeatedly with cold 2-propanol and dried under vacuum to yield 12.9 g (84 %) of 4-(diethylamino)salicylaldehyde N-methyl-N-phenylhydrazone. The melting point was found to be 75.5-76.5 °C (recrystallized from 2-propanol). The ¹H-NMR spectrum (100 Mhz) of the product in CDCl₃ was characterized by the following chemical shifts (in ppm): 11.53 (s, 1H, OH); 7.63 (s, 1H, N=CH); 7.50-6.80 (m, 6H, Ar); 6.26 (m, 2H, Ar); 3.37 (m, 7H, CH₂CH₃, NCH₃); 1.18 (t, 6H, CH₂CH₃, J= 7.0 Hz). An elemental analysis yielded the following results in weight percent: C 72.61; H 7.88; N 14.20, which compared with calculated values for C₁₈H₂₃N₃O in weight percent of: C 72.70; H 7.80; N 14.13.

Preparation of 9-ethylcarbazole-3,6-dicarbaldehyde bis(N-2,3-epoxypropyl-N-phenyl)hydrazone

A 271 ml quantity of dimethylformamide (DMF, 3.5 mol) was added to a 1-liter, 3-neck round bottom flask equipped with a mechanical stirrer, a thermometer, and an addition funnel. The contents were cooled in a salt/ice bath. When the temperature inside the flask reached 0 °C, 326 ml of phosphorus oxychloride (POCl₃, 3.5 mol) was slowly added. During the addition of POCl₃, the temperature inside the flask was not allowed to rise above 5 °C. After the addition of POCl₃, the reaction mixture was allowed to warm to room temperature. After the flask warmed to room temperature, N-ethylcarbazole (93 g) in 70 ml of DMF was added and then the flask was heated to 90 °C for 24 hours using a heating mantle. Next, the reaction mixture was cooled to room temperature and the reaction mixture was added slowly to a cooled 4.5 liter beaker containing a solution comprising 820 g of sodium acetate dissolved in 2 liters of water. The beaker was cooled in an ice bath and stirred for 3 hours. The brownish solid obtained was filtered and washed repeatedly with water, followed by a small amount of

ethanol (50 ml). After washing, the resulting product was recrystallized once from toluene using activated charcoal and dried under vacuum in an oven heated at 70 °C for 6 hours to obtain 55 g (46% yield) of N-ethyl-3,6-diformylcarbazole. The ¹H-NMR spectrum (250 MHz) of the product in CDCl₃ was characterized by the following
5 chemical shifts (δ, ppm): 10.12 (s, 2H); 8.63 (s, 2H); 8.07 (d, 2H); 7.53 (d, 2H); 4.45 (m, 2H); 1.53 (t, 3H).

Phenylhydrazine (0.2 mole, commercially available from Aldrich, Milwaukee, WI) and N-ethyl-3,6-diformylcarbazole (0.1 mole) were dissolved in 100 ml of a 1:1 v/v mixture of toluene and THF in 250 ml 3-neck round bottom flask equipped with a reflux
10 condenser and a mechanical stirrer. The solution was refluxed for 2 hours. Thin layer chromatography indicated the disappearance of the starting materials. At the end of the reaction, the mixture was cooled to room temperature. The N-ethyl-3,6-diformylcarbazole bis(N-phenylhydrazone) crystals formed upon standing were filtered off, washed with isopropanol and dried in a vacuum oven at 50 °C for 6 hours. Without
15 further purification, the product was used for the next step.

A mixture of N-ethyl-3,6-diformylcarbazole bis(N-phenylhydrazone) (4.3 g, 0.01 mole), 85% powdered potassium hydroxide (2.0 g, 0.03 mole) and anhydrous potassium carbonate in 25 ml of epichlorohydrin was stirred vigorously at 55-60 °C for 1.5-2 hours. The course of the reaction was monitored using thin layer chromatography on silica gel
20 60 F254 plates (commercially available from Merck) using a 1:4 v/v mixture of acetone and hexane as eluant. After termination of the reaction, the mixture was cooled to room temperature, diluted with ether, and washed with water until the wash water had a neutral pH. The organic layer was dried over anhydrous magnesium sulfate, treated with activated charcoal, and filtered. Ether was removed and the residue was purified by
25 recrystallization from toluene followed by column chromatography (silica gel Merck grade 9385, 60 Å, Aldrich; 4:1 v/v solution of hexane and acetone as the eluant). The yield of the product, 9-ethylcarbazole-3,6-dicarbaldehyde bis(N-2,3-epoxypropyl-N-phenyl)hydrazone was 68.5 % and had a melting point of 119-120 °C (recrystallized from toluene). The ¹H-NMR spectrum (100 MHz) of the product
30 in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 8.5-7.8 (m, 8H); 7.6-7.2 (m, 8H); 7.0 (m, 2H); 4.55 (m, 6H); 3.3 (m, 2H); 2.9 (dd, 2H); 2.65 (dd, 2H); 1.4

(t, 3H). An elemental analysis yielded the following values in weight %: C 75.01; H 6.91; N 12.68. For comparison the calculated elemental weight percents for $C_{41}H_{46}N_6O_2$ are %: C 75.20; H 7.08; N 12.83.

5 Preparation of 4,4'-diformyltriphenylamine bis(N-2,3-epoxy-propyl-N-phenylhydrazone)

Dimethylformamide (DMF, 271 ml, 3.5 mol, obtained from Aldrich, Milwaukee, WI) was added to a 1-liter 3-neck round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel. The DMF in the flask was cooled on an ice bath with salt. When the temperature inside the flask reached 0 °C, phosphorous
 10 oxychloride ($POCl_3$, 326 ml, 3.5 mol, available from Aldrich, Milwaukee, WI) was added slowly to the flask through a dropping funnel. During the addition of $POCl_3$, the temperature inside the flask was not allowed to rise above 5 °C. After the addition of $POCl_3$ was completed, the reaction mixture was allowed to warm to room temperature. Triphenylamine (127 g, 0.5 mole, obtained from Aldrich, Milwaukee, WI) was added and
 15 then the flask was heated to 90 °C for 24 hours using a heating mantle. After the reaction mixture was cooled to room temperature, it was added slowly to a 4.5 liter beaker containing a solution of 820 g of sodium acetate dissolved in 2 liters of water. The beaker was stirred and cooled on an ice bath for 3 hours. The resulting brownish solid was filtered and washed repeatedly with water and finally with a small amount of ethanol
 20 (50 ml). The resulting product, 4-(4-formyldiphenylamino)benzaldehyde, was recrystallized once from a mixture of toluene and isopropanol using activated charcoal and dried under vacuum in an oven heated at 50 °C for 6 hours. The yield was 86 g (55 %).

4-(4-Formyldiphenylamino)benzaldehyde (60 g, 0.2 mol, prepared in previous
 25 step) and 250 ml of tetrahydrofuran were added to a 500 ml 2-neck round-bottomed flask equipped with a reflux condenser and a mechanical stirrer. The mixture was heated until the solids were dissolved. Then, a solution of 47 ml of N-phenylhydrazine (0.5 mol, obtained from Aldrich, Milwaukee, WI) in 50 ml of tetrahydrofuran was added slowly using a dropping funnel. The flask was refluxed until 4-(4-formyldiphenylamino)
 30 benzaldehyde disappeared (~10 min). At the end of the reaction, the mixture was cooled slowly to room temperature, and the solid was filtered off, washed with isopropanol, and

dried at 30 °C under vacuum for 6 hours. The product was 4-(4-formyldiphenylamino)benzaldehyde bis(N-phenyl)hydrazone. The yield was 80 g (84 %).

4-(4-Formyldiphenylamino)benzaldehyde bis(N-phenyl)hydrazone (77 g of 0.16 mol, prepared in previous step) and epichlorohydrin (283 ml, 3.6 mol, obtained from Aldrich, Milwaukee, WI) were added to a 1000 ml 3-neck round-bottomed flask equipped with a reflux condenser, a thermometer, and a mechanical stirrer. The reaction mixture was stirred vigorously at 35-40 °C for 7 hours. During the time in which the reaction mixture was stirred, powdered potassium hydroxide (85 %, 79 g, 1.2 mol) and anhydrous sodium sulfate (18.1 g, 0.14 mol) were added in three portions while the reaction mixture was kept at 20-25 °C. After the termination of the reaction, the mixture was cooled to room temperature and filtered. The organic phase was treated with diethyl ether and washed with distilled water until the pH of the washed water was neutral. The organic phase was dried over anhydrous magnesium sulfate, treated with activated charcoal, and filtered. The solvents were removed by evaporation and the residue was dissolved in 90 ml of toluene. The crystals that formed upon standing were filtered off and washed with 2-propanol to yield 45 g (47 %) of 4-(4-formyldiphenylamino)benzaldehyde bis(N-2,3-epoxypropyl-N-phenyl)hydrazone. The melting point was found to be 163.5-165 °C (recrystallized from toluene). The ¹H-NMR spectrum (100 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 7.8-6.8 (m, 25H, Ar); 4.5-4.2 (dd, 2H, one proton of NCH₂); 4.1-3.8 (dd, 2H, another proton of NCH₂); 3.2 (m, 2H, CH); 2.8 (dd, 2H, one proton of OCH₂); and 2.7-2.5 (dd, another proton of OCH₂). An elemental analysis yielded the following results in weight percent: C 76.71; H 5.91; N 11.70. For comparison the calculated elemental weight percents for C₃₈H₃₅N₅O₂ are: C 75.20; H 7.08; N 12.83. C 76.87; H 5.94; N 11.80.

Compound (1)

A mixture of 9-ethylcarbazole-3,6-dicarbaldehyde bis(N-2,3-epoxypropyl-N-phenyl)hydrazone (prepared above, 4.5 g, 8.3 mmol), 4-(diethylamino)salicylaldehyde N-methyl-N-phenylhydrazone (prepared above, 6.17 g, 20.7 mmol), 4-(dimethylamino)-pyridine (1.01 g, 8.3 mmol, obtained from Aldrich), and 25 ml of 1,4-dioxane was added

to a 100 ml round bottom flask equipped with a reflux condenser and a mechanical stirrer. After the reaction mixture was refluxed for 5 hours, the solvent was evaporated and the crude product was purified by column chromatography (silica gel, grade 62, 60-200 mesh, 150 Å, Aldrich) using a mixture of acetone and hexane in a volume ration of 3:22 as an eluent. Fractions containing the product were collected and evaporated. The product was recrystallized from toluene. The yield of the product was 4.6 g (49 %). The melting point of the product was found to be 131-133 °C. The ¹H-NMR spectrum (250 MHz) of the product in CDCl₃ was characterized by the following chemical shifts (δ, ppm): 8.17 (s, 2H, N=CH attached to Ht); 7.88-7.72 (m, 8H, 6-H of 1,2,4-subst. Ph, other N=CH, Ht); 7.46-7.06 (m, 18H, Ar); 6.93 (m, 2H, 4-H of Ph); 6.77 (m, 2H, 4-H of other Ph); 6.30 (d, split, 2H, 5-H of 1,2,4-subst. Ph); 6.08 (s, split, 2H, 3-H of 1,2,4-subst. Ph); 4.54-4.40 (m, 2H, CH); 4.34-3.98 (m, 10H, NCH₂CH₃ attached to Ht, NCH₂CHCH₂O); 3.32-3.15 (m, 14H, NCH₃, other NCH₂CH₃); 3.11 (d, 2H, OH); 1.36 (t, 3H, NCH₂CH₃ attached to Ht, *J*= 7.0 Hz); 1.03 (t, 12H, other NCH₂CH₃, *J*= 7.0 Hz). An elemental analysis yielded the following results in weight percent: C 73.71; H 6.92; N 13.74, which compared with calculated values for C₇₀H₇₉N₁₁O₄ in weight percent of: C 73.85; H 6.99; N 13.53.

Compound (2)

A mixture of 4,4'-diformyltriphenylamine bis(N-2,3-epoxy-propyl-N-phenylhydrazone) (5 g, 8.4 mmol), bis(4,4'-diethylamino)salicylaldehyde-N,N-diphenylhydrazone (7.5 g, 21 mmol), 4-(dimethylamino)-pyridine (1.03 g, 8.4 mmol, obtained from Aldrich), and 25 ml of 1,4-dioxane was added to a 100 ml 3-neck round bottom flask, equipped with a reflux condenser and a mechanical stirrer. After the mixture was refluxed for 12 hours, the solvent was evaporated. The crude product was purified by column chromatography (silica gel, grade 62, 60-200 mesh, 150 Å, Aldrich) using a mixture of acetone and hexane in a volume ration of 1:4 as an eluent. Fractions containing the product were collected and evaporated. The oily residue was dissolved in toluene to form a 20% solution. The solution was poured with intensive stirring into a fifteen-fold excess of *n*-hexane. The resulted precipitate was filtered off, washed repeatedly with hexane and dried under vacuum at 50 °C to yield Compound (2). The yield was 6.2 g (56.1%). The ¹H-NMR spectrum (250 MHz) of the product in CDCl₃ was

characterized by the following chemical shifts (δ , ppm): 7.78 (d, 2H, 6-H of 1,2,4-subst. Ph, $J=8.8$ Hz); 7.47 (s, 2H, CH=N); 7.45-6.84 (m, 45H, other N=CH, Ar); 6.30 (d, split, 2H, 5-H of 1,2,4-subst. Ph, $J=8.8$ Hz); 5.95 (s, split, 2H, 3-H of 1,2,4-subst. Ph); 4.20-4.05 (m, 2H, CH₂CHCH₂); 3.95-3.62 (m, 8H, CH₂CHCH₂); 3.24 (q, 8H, CH₂CH₃, $J=7.0$ Hz); 2.51 (d, 2H, OH, $J=5.8$); 1.04 (t, 12H, CH₂CH₃, $J=7.0$ Hz). An elemental analysis yielded the following results in weight percent: C 76.62; H 6.58; N 11.93, which compared with calculated values for C₈₄H₈₅N₁₁O₄ in weight percent of: C 76.86; H 6.53; N 11.74.

10 Example 2 - Charge Mobility Measurements

This example describes the measurement of charge mobility and ionization potential for charge transport materials, specifically Compounds (1) - (2) above.

Sample 1

15 A mixture of 0.1 g of the Compound (1) and 0.1 g of polyvinylbutyral (S-LEC B BX-1, commercially obtained from Sekisui) was dissolved in 2 ml of tetrahydrofuran (THF). The solution was coated on a polyester film with a conductive aluminum layer by a dip roller. After the coating was dried for 1 hour at 80 °C, a clear 10 μ m thick layer was formed. The hole mobility of the sample was measured and the results are presented
20 in Table 1.

Sample 2

Sample 2 was prepared and tested similarly as Sample 1, except polycarbonate Z replaced polyvinylbutyral.

25

Sample 3

Sample 3 was prepared and tested similarly as Sample 2, except Compound (2) replaced Compound (1).

30

Sample 4

Sample 4 was prepared and tested similarly as Sample 3, except polycarbonate Z was not used.

5 Mobility Measurements

Each sample was corona charged positively up to a surface potential U and illuminated with 2 ns long nitrogen laser light pulse. The hole mobility μ was determined as described in Kalade et al., "Investigation of charge carrier transfer in electrophotographic layers of chalcogenide glasses," Proceeding IPCS 1994: The Physics and Chemistry of Imaging Systems, Rochester, NY, pp. 747-752, incorporated herein by reference. The hole mobility measurement was repeated with appropriate changes to the charging regime to charge the sample to different U values, which corresponded to different electric field strength inside the layer E. This dependence on electric field strength was approximated by the formula

$$\mu = \mu_0 e^{\alpha \sqrt{E}}.$$

Here E is electric field strength, μ_0 is the zero field mobility and α is Pool-Frenkel parameter. Table 1 lists the mobility characterizing parameters μ_0 and α values and the mobility value at the 6.4×10^5 V/cm field strength as determined by these measurements for the four samples.

Table 1

Sample	μ_0 (cm ² /V·s)	μ (cm ² /V·s) at $6.4 \cdot 10^5$ V/cm	α (cm/V) ^{0.5}	Ionization Potential (eV)
Compound (1)	/	/	/	5.12
Sample 1	3.3×10^{-10}	6.0×10^{-8}	0.0065	/
Sample 2	1.2×10^{-9}	5.0×10^{-7}	0.0076	/
Compound (2)	/	/	/	5.17
Sample 3	5.0×10^{-9}	1.7×10^{-7}	0.0044	/
Sample 4	4.7×10^{-8}	2.0×10^{-5}	0.0076	/

Example 3 - Ionization Potential Measurements

This example describes the measurement of the ionization potential for the 2 charge transport materials described in Example 1.

To perform the ionization potential measurements, a thin layer of charge transport
5 material about 0.5 μm thickness was coated from a solution of 2 mg of charge transport material in 0.2 ml of tetrahydrofuran on a 20 cm^2 substrate surface. The substrate was an aluminized polyester film coated with a 0.4 μm thick methylcellulose sub-layer.

Ionization potential was measured as described in Grigalevicius et al., "3,6-Di(N-diphenylamino)-9-phenylcarbazole and its methyl-substituted derivative as novel hole-
10 transporting amorphous molecular materials," *Synthetic Metals* **128** (2002), p. 127-131, incorporated herein by reference. In particular, each sample was illuminated with monochromatic light from the quartz monochromator with a deuterium lamp source. The power of the incident light beam was $2.5 \cdot 10^{-8}$ W. A negative voltage of -300 V was supplied to the sample substrate. A counter-electrode with the 4.5×15 mm^2 slit for
15 illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of a BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. A $10^{-15} - 10^{-12}$ amp photocurrent was flowing in the circuit under illumination. The photocurrent, I , was strongly dependent on the incident light photon energy $h\nu$. The $I^{0.5} = f(h\nu)$ dependence was plotted. Usually, the
20 dependence of the square root of photocurrent on incident light quanta energy is well described by linear relationship near the threshold (see references "Ionization Potential of Organic Pigment Film by Atmospheric Photoelectron Emission Analysis," *Electrophotography*, 28, Nr. 4, p. 364 (1989) by E. Miyamoto, Y. Yamaguchi, and M. Yokoyama; and "Photoemission in Solids," *Topics in Applied Physics*, **26**, 1-103 (1978)
25 by M. Cordona and L. Ley, both of which are incorporated herein by reference). The linear part of this dependence was extrapolated to the $h\nu$ axis, and the I_p value was determined as the photon energy at the interception point. The ionization potential measurement has an error of ± 0.03 eV. The ionization potential values are given in Table 1 above.

As understood by those skilled in the art, additional substitution, variation among substituents, and alternative methods of synthesis and use may be practiced within the scope and intent of the present disclosure of the invention. The embodiments above are intended to be illustrative and not limiting. Additional embodiments are within the claims.

- 5 Although the present invention has been described with reference to particular embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.